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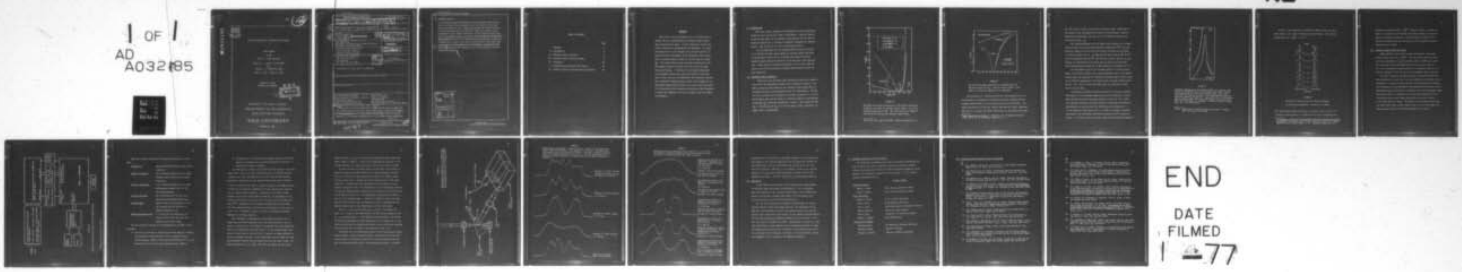

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RESONANT RAMAN EFFECT IN CRYSTALS AND LIQUIDS

FINAL REPORT

to the

OFFICE OF NAVAL RESEARCH

Contract No. N00014-67-A-0097-0005

and

Contract No. N00014-75-C-0866

April 1, 1967 - August 31, 1976

Richard K. Chang

Principal Investigator

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REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER (9) Final rept. 1 apr 67-31 Aug 76	2. GOVT ACCESSION NO. / 3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) (6) RESONANT RAMAN EFFECT IN CRYSTALS AND LIQUIDS.	5. TYPE OF REPORT & PERIOD COVERED Final 4/1/67 - 8/31/76
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) (10) Richard K. Chang (Yale University)	8. CONTRACT OR GRANT NUMBER(s) (15) N00014-67-A-0097-0005, and ONR N00014-75-C-0866
9. PERFORMING ORGANIZATION NAME AND ADDRESS Yale University Department of Engineering and Applied Science New Haven, Connecticut 06520	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR-396-018
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Physical Sciences Division Arlington, Virginia 22217	12. REPORT DATE (11) Oct 76 / 13. NUMBER OF PAGES 19
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Office of Naval Research New York Area Office 715 Broadway New York, New York 10003 (12) 23 p.	15. SECURITY CLASS. (of this report) Unclassified / 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

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17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Resonant Raman scattering	Direct energy gap
Electron-phonon deformation potential	Indirect energy gap
Fröhlich interaction	Semiconductors
Second-order Raman scattering	Gas concentration profile
Raman scattering cross section	Ultra low light level television camera

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The first of two main objectives in ~~our~~ this research was to further the basic understanding of resonance Raman scattering in solids and in gases. ~~In this connection, we were the first to observe~~ the following two new phenomena were observed: (1) resonant cancellation in the TO Raman cross section; and

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20. ABSTRACT (Cont'd).

(2) selective resonant enhancement in the two-phonon cross section when the incident photon energy is near the indirect energy gap. The second objective was to design and develop an optical parallel-channel detection system for ultra-low light level spectroscopy. In addition to the obvious improvement in the signal-to-noise ratio and in the speed of acquiring data, ~~we were the first to demonstrate that~~ spatially resolved gas concentration emerging from a nozzle can be mapped out by using laser Raman intensity from a one 1 msec ruby laser pulse. ~~As a by-product of this research, we believe we have~~ This is introduced a totally new diagnostic tool for the study of gas and combustion dynamics.

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TABLE OF CONTENTS

ABSTRACT

The first of two main objectives in our research was to further the basic understanding of resonance Raman scattering in solids and in gases. In this connection, we were the first to observe the following two new phenomena: (1) resonant cancellation in the TO Raman cross section; and (2) selective resonant enhancement in the two-phonon cross section when the incident photon energy is near the indirect energy gap. The second objective was to design and develop an optical parallel-channel detection system for ultra-low light level spectroscopy. In addition to the obvious improvement in the signal-to-noise ratio and in the speed of acquiring data, we were the first to demonstrate that spatially resolved gas concentration emerging from a nozzle can be mapped out by using laser Raman intensity from a one 1 msec ruby laser pulse. As a by-product of this research, we believe we have introduced a totally new diagnostic tool for the study of gas and combustion dynamics.

I. INTRODUCTION

This final report summarizes the highlights of work accomplished during the nine and one-half years of ONR support. Specific details on the various phases of our research investigations can be found in Technical Reports Nos. 1 through 21 submitted throughout the contract period. (See Section VI for list of individual titles.)

The two main goals of our research endeavors were as follows: 1) To further the basic understanding of resonance Raman scattering in solids and in gases; and 2) to design and develop an optical parallel-channel detection system for ultra-low light level spectroscopy. Other research activities presented in some of the technical reports were either by-products of and/or necessitated by these two main objectives.

II. RESONANCE RAMAN SCATTERING

During the past ten years, many laboratories have been engaged in theoretical and experimental studies of the resonance behavior of the Raman scattering cross section as the incident photon energy ($\hbar\omega_i$) is increased from below the absorption gap of the semiconductor. We were the first to report the existence of a resonant cancellation in the TO phonon Raman cross section as $\hbar\omega_i$ is increased toward the semiconductor energy gap (E_g) [Technical Reports Nos. 3 and 6]. The results for CdS (E_g = 2.58 eV) and ZnS (E_g = 3.9 eV) are shown in Fig. 1 and Fig. 2 on pages 3 and 4, respectively.

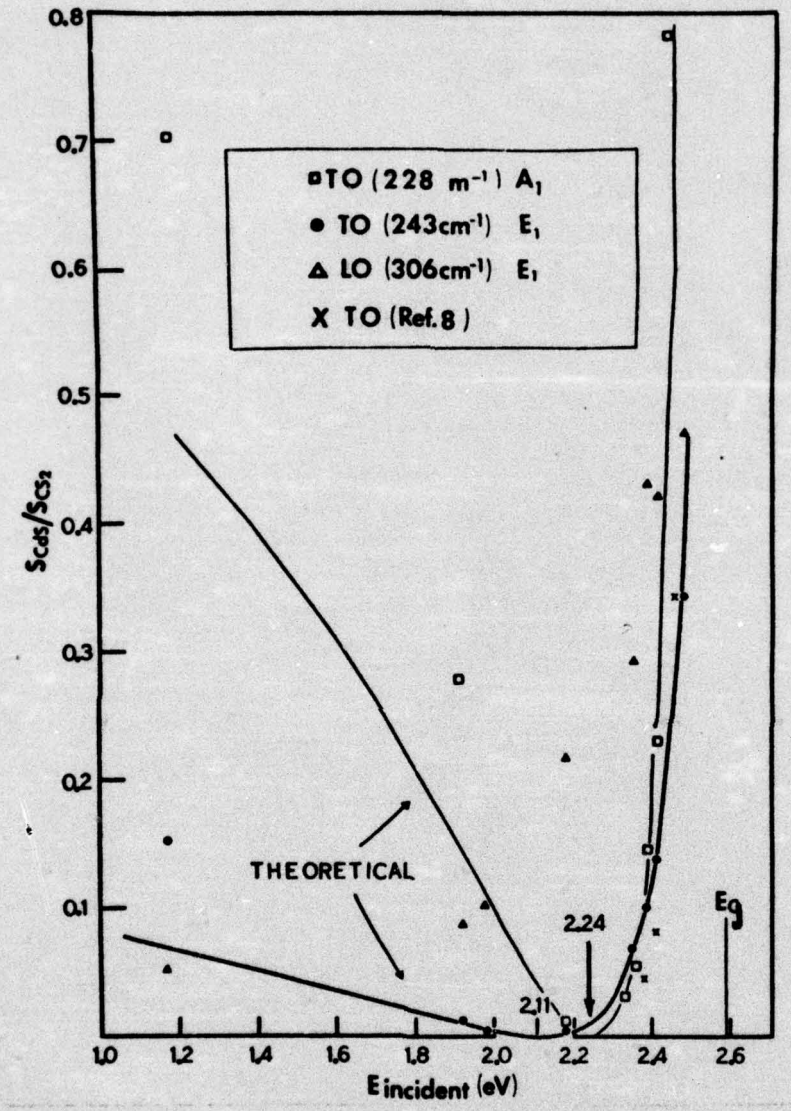

FIGURE 1*

The Raman scattering efficiencies of CdS (80°K) normalized to CS_2 as a function of incident photon energy. E_g is the electron energy gap of CdS. The solid curves are computed from existing free-electron resonant Raman theory.

*Phys. Rev. Lett. 25, 814 (1970) [Technical Report No. 3].

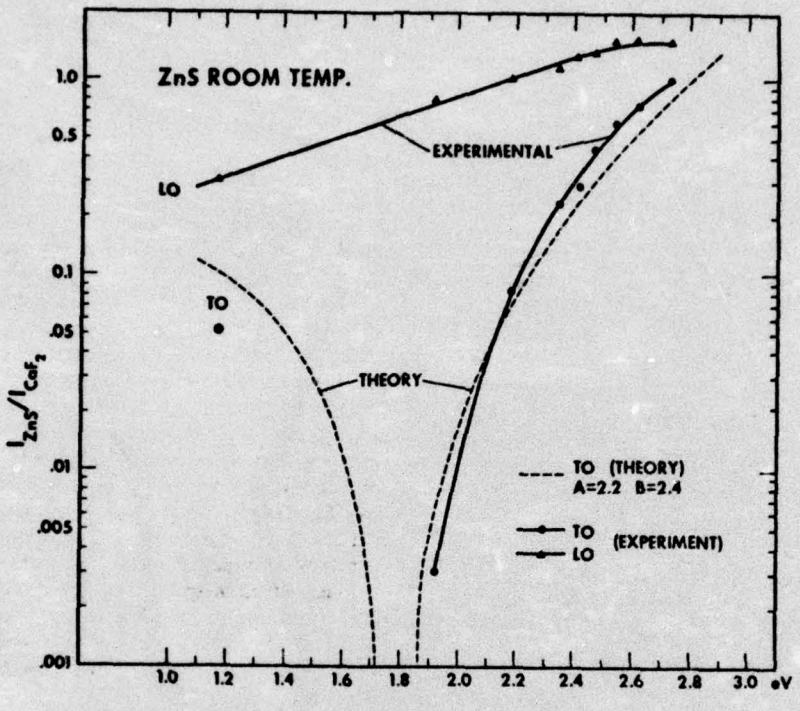

FIGURE 2*

The LO and TO Raman dispersions of hexagonal ZnS normalized to that of CaF_2. Crystals were at 300°K. Data point at 1.17 eV was measured by A. Mooradian.

The existence of a resonant cancellation was proposed by us as a manifestation of a destructive interference between resonant and non-resonant contributions to the TO Raman scattering cross section. The former contribution is from the valence bands and the lowest conduction band near K = 0, while the latter contribution is from these same bands

*Light Scattering in Solids, M. Balkanski, ed. (Flammarion Sciences, Paris, 1971), p. 41. [Technical Report No. 6]

but with $K \neq 0$, as well as from other electronic bands. Depending on the relative sign and magnitude of these two contributions, complete destructive interference can give rise to the observed resonant cancellation for $\hbar\omega_i < E_g$.

The interrelationship of the TO Raman cross section, the LO Raman cross section, the optical second harmonic coefficient (d^{NL}), and the effective charge (e^*) associated with lattice vibration was discussed in Technical Report No. 16. By combining the known sign of d^{NL} and e^* with our dispersion data on d^{NL}, the TO cross section, and the LO cross section, we postulated for the first time the sign of the electron-phonon (hole-phonon) interaction in CdS and ZnS for TO phonons at $K = 0$.

Our experimental data on the resonant behavior of the LO phonon Raman cross section (one-LO, n-LO, and forbidden-LO) over a wide photon energy range were important for subsequent resonant Raman theories based on the Fröhlich interaction of LO phonons with electrons [Technical Report No. 11]. Fig. 3 on the next page shows the comparison of such theory with our data.

We recently reported the first observation of selective resonant enhancement in the two-phonon Raman spectrum of Si when $\hbar\omega_i$ is coincident with the Si indirect band gap [Technical Report No. 15]. Under this resonant condition, the electron-phonon interaction involving the scattering of an electron from the conduction band minimum at $K = 0$ to the conduction band minima at $K = \Delta = 0.85X$ is resonantly enhanced. Furthermore, the hole-phonon interaction involving a hole scattering from $K = \Delta = 0.85X$ to the $K = 0$ valence band is also resonantly enhanced.

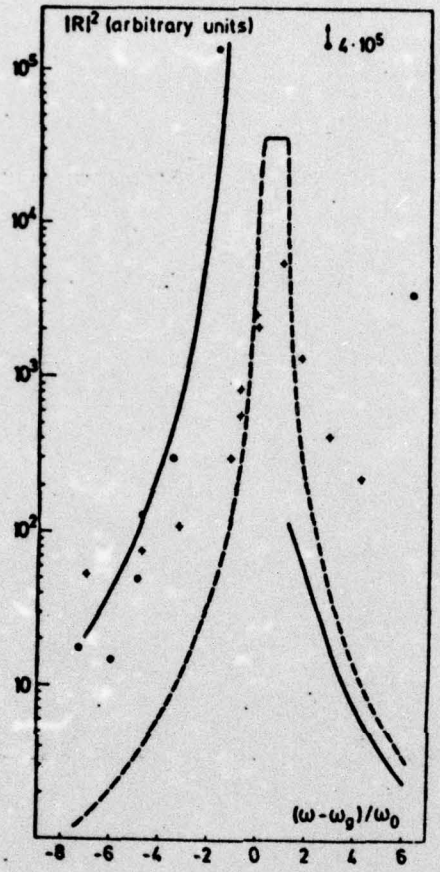

FIGURE 3*

Frequency dependence of the squared modulus of a nonzero component of the Raman tensor for forbidden scattering. Dashed curve calculated for free electron-hole pairs, solid curve calculated for Wannier excitons. The experimental points are from the following references: Crosses for GaP, B.A. Weinstein and M. Cardona, Phys. Rev. B 8, 2795 (1973); open circles for CdS, R.H. Callender, S.S. Sussman, M. Selders, and R.K. Chang, Phys. Rev. B 7, 3788 (1973).

*From: Roland Zeyher, Chin-Sen Ting, and Joseph L. Birman, Phys. Rev. B 10, 1725 (1974).

In Fig. 4, the dependence of 2TA(X) and 2TO(Δ) on $\hbar\omega_i$ is shown with respect to all other two-phonon Raman scattering. The indirect energy gap of Si is E_g^{ind} = 1.17 eV.

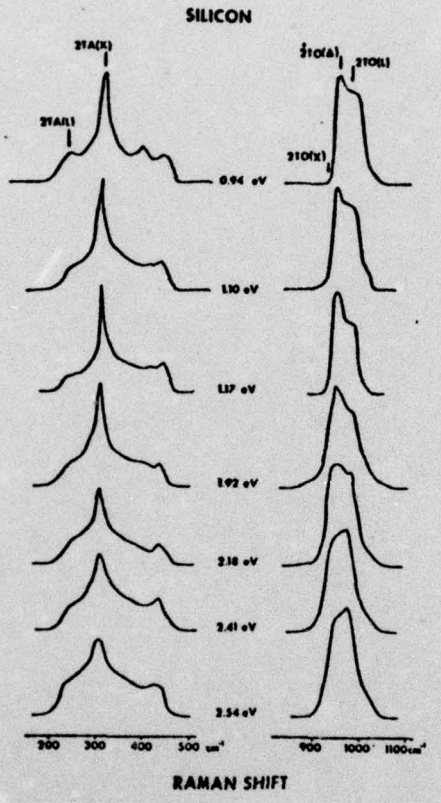

FIGURE 4*

Evolution of 2TA and two-optic phonon lineshape in Si with increasing $\hbar\omega$. Crystal was at 300°K.

Only those phonons that can scatter an electron from K = 0 to K = Δ = 0.85X or a hole from K = Δ = 0.85X to K = 0 can, in principle, be

* Proceedings of the Third International Conference on Light Scattering in Solids, M. Balkanski, R.C.C. Leite, and S.P.S. Porto, eds. (Flammarion Sciences, Paris, 1976), p. 93. [Technical Report No. 18]

resonantly enhanced when $\hbar\omega_i \simeq E_g^{ind}$. Presently, under a new ONR contract, we are pursuing the resonant two-phonon studies as a possible means of providing information on electron-phonon interaction for electron scattering from the zone center to $K \neq 0$ minima or between equivalent $K \neq 0$ minima.

III. PARALLEL-CHANNEL DETECTION SYSTEM

Raman radiation from solids is weak, particularly from opaque crystals ($\hbar\omega_i \geq E_g$ or $\hbar\omega_i \geq E_g^{ind}$). The total time needed to acquire the entire wavelength is long (typically 1,000 to 10,000 sec), while the time spent at each wavelength interval is only 10 to 100 sec. When one is detecting the Raman photons in a wavelength interval, intensity information from the rest of the wavelength range is ignored.

In order to improve the signal-to-noise ratio and the speed for data acquisition, we some five years ago embarked on the design and development of a parallel-channel detection system (PCDS) which combines the advantages of a photomultiplier (quantum-limited detection) and of a photographic plate (simultaneous recording over a wide wavelength range). The optimum choice of components was at that time determined to be a three-stage electrostatic image intensifier fiber-optics coupled to an image isocon TV camera. The details of our computer controlled, low light level camera system, shown in Fig. 5 on the next page, have been presented earlier in Technical Reports Nos. 14 and 17.

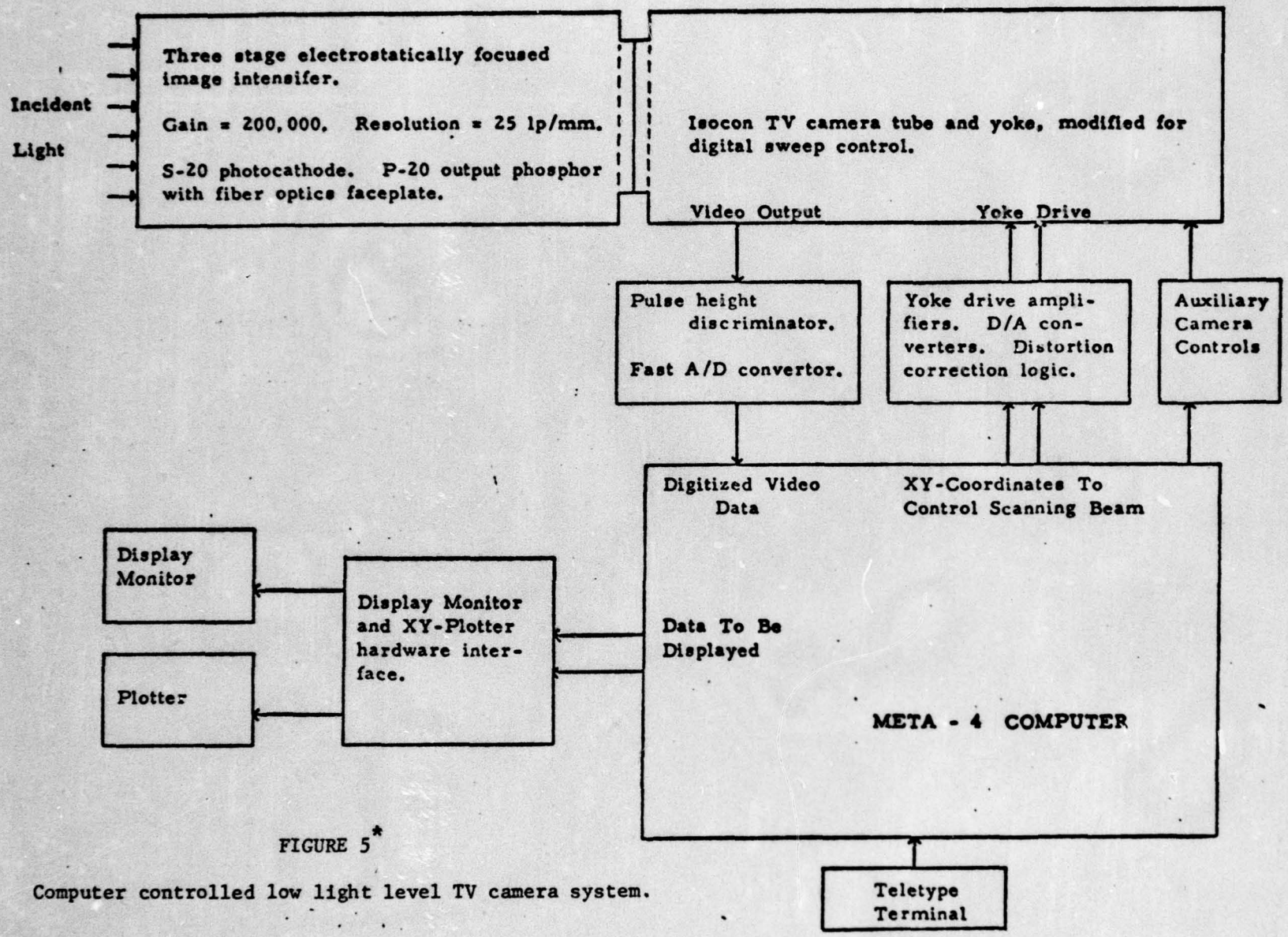

FIGURE 5*

Computer controlled low light level TV camera system.

*Technical Reports Nos. 14 and 17.

Thus far, we have achieved the following characteristics for the PCDS:

Sensitivity:	Quantum-limited detection (single photo-electron).
Spatial resolution:	125 resolvable elements over the 30 mm diameter under ultra-low light level conditions.
Spectral resolution:	2 to 3 Å when used with a 3/4-m double spectrograph equipped with two 1800 grooves/mm gratings.
Spectral coverage:	60 to 90 Å when used with the above-mentioned spectrograph and gratings.
Dynamic range:	1000:1 without the selective scan format proposed for the first time in Technical Report No. 14.
Target integration time:	2 to 3 sec for the cooled isocon TV camera (-20°C), while 20 to 30 min is expected for the SEC camera.

The two innovative features we have designed into our PCDS are the following:

1) Selective scan format to increase the dynamic range by "reading" more frequently those portions of the TV target which have stored a greater number of photo-electrons (brighter) than those portions which have stored fewer photo-electrons (darker).

2) Incorporation of a commercially available geometric correction module to compensate the pin-cushion distortions caused by the electrostatic image intensifier.

Our PCDS has been computer controlled and fully operative only since August 1976. Compared to the conventional manner of taking data with a spectrometer and a photomultiplier, we find that the PCDS provides significant improvements in the signal-to-noise ratio and a reduction in data-acquisition time--that is, we now can measure the Raman spectrum in 1/125 [(# of resolvable elements)$^{-1}$] of the original time required for the single-channel technique. Conversely, if we used the same length of time as the single-channel technique, the improvement of the signal-to-noise ratio is a factor 10 to 11 times [(# of resolvable elements)$^{1/2}$]. Furthermore, by recording the Raman data with the PCDS, the total Raman spectrum is insensitive to fluctuations in the laser intensity and, consequently, there is no need to renormalize different segments of the Raman spectrum.

The advantages of recording the entire Raman spectrum on the TV target are particularly apparent when a low repetition pulse laser is used as a laser source. For example, a Q-switched ruby laser pumped dye laser can be fired only once every 30 sec. By the single-channel technique, it would take at least 3750 sec to measure the Raman intensity at the 125 wavelength interval. On the other hand, with the PCDS, the same 125 wavelength interval can be measured with only one laser firing. For many semiconductors (e.g., CdTe, GaAs, InP, and CdSe), the only laser

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sources with $\hbar\omega_i \approx E_g$ are those from a Q-switched ruby laser pumped dye laser (7,000 to 11,000 Å). Some of the investigations pertinent to the new ONR contract will require the use of such dye lasers and the PCDS.

The most striking and unique feature of the PCDS is the ability to spatially resolve the Raman intensity at a fixed wavelength interval--that is, by setting the spectrograph at the peak of the Raman signal, the PCDS can be made to measure the spatial distribution of that Raman intensity. To demonstrate the significance of this feature, we have recently applied our PCDS to the measurement of the concentration profile of a gas jet emerging from a nozzle (dia 1.5 mm) with a wire (dia 0.25 mm or 0.13 mm) in front of it. The experimental configuration is shown in Fig. 6 on the following page. A vertical cylindrical strip (3 mm long and about 100 μ dia) of the concentration profile is resolved into 125 spatial elements and is recorded during one 1 msec laser pulse.

The gas we have used is either O_2 or Freon-12. By setting the double spectrograph on the Raman peak of the gas, we have mapped out the gas concentration profile at some distance from the nozzle. By setting the double spectrograph on the N_2 Raman peak, we have mapped out the air profile and observed the mixing zone between the air and the gas emerging from the nozzle with or without a wire placed in front of it.

We believe that our preliminary results on the concentration profile (shown in Figs. 7 and 8 on pages 14 and 15, respectively) are the first of their kind. All previous results using hot-wire probes can map out only the velocity profile and not the concentration profile. Schlieren

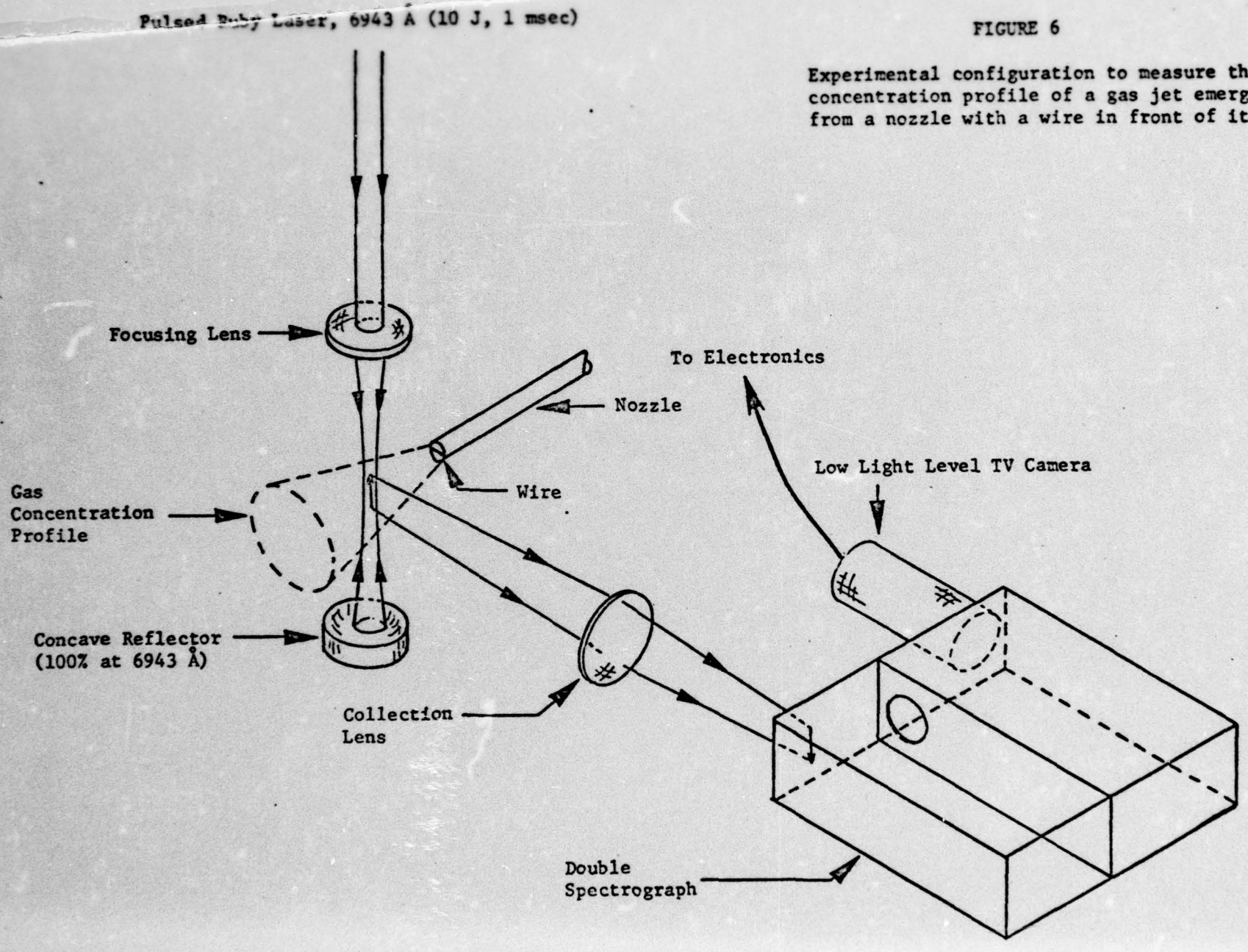


FIGURE 6

Experimental configuration to measure the concentration profile of a gas jet emerging from a nozzle with a wire in front of it.

FIGURE 7

Experimental arrangement is shown in Fig. 6. Nozzle is 1.52 mm in diameter, 152.4 mm in length. Wire diameter is 0.127 mm. Gas pressure at the entrance end of the nozzle is 40 PSIG. Gas used is Freon-12 (CCl_2F_2) which has a Raman vibration at 667 cm^{-1}. A - E are the spatially resolved concentration profiles as determined from the Raman intensity of Freon-12.

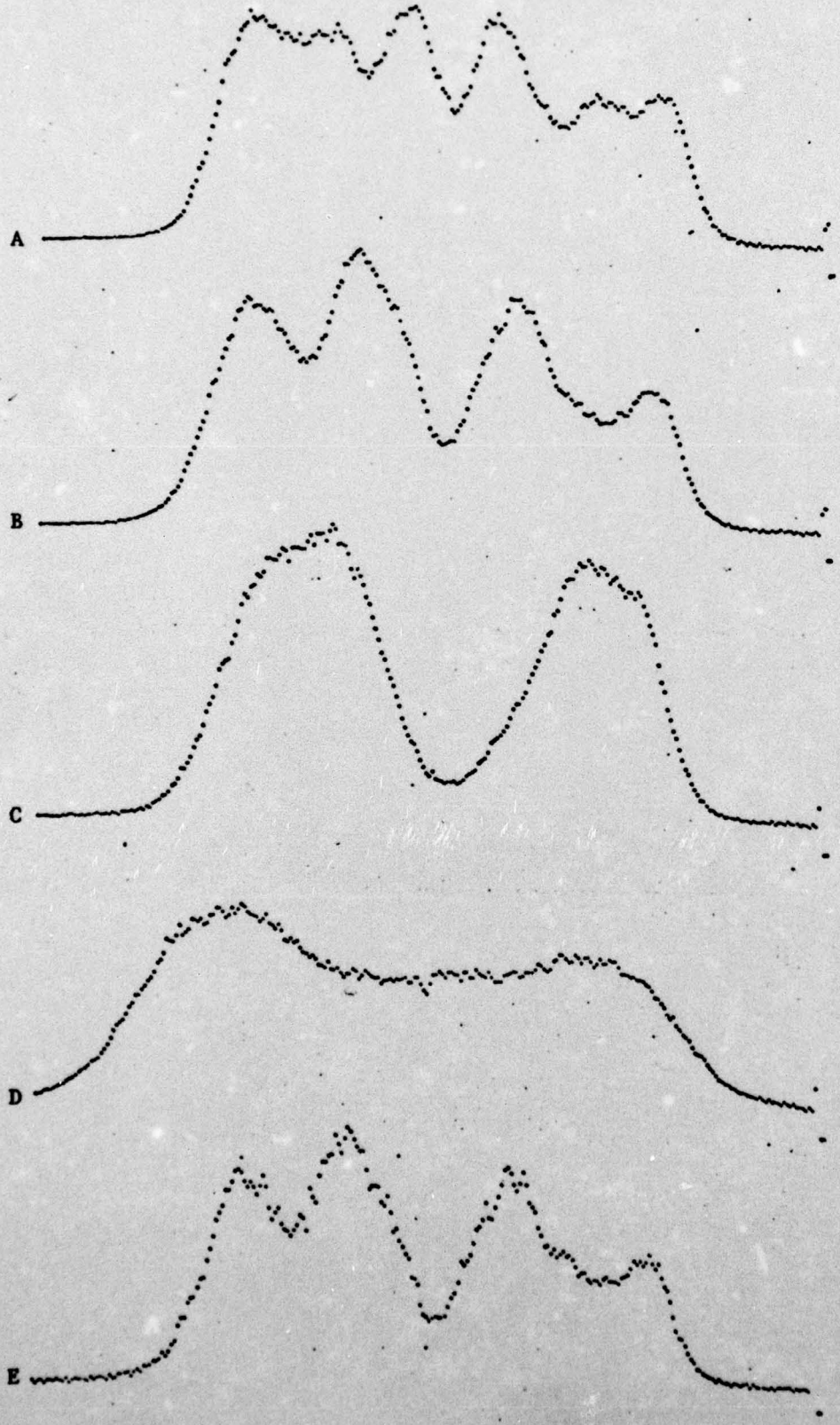
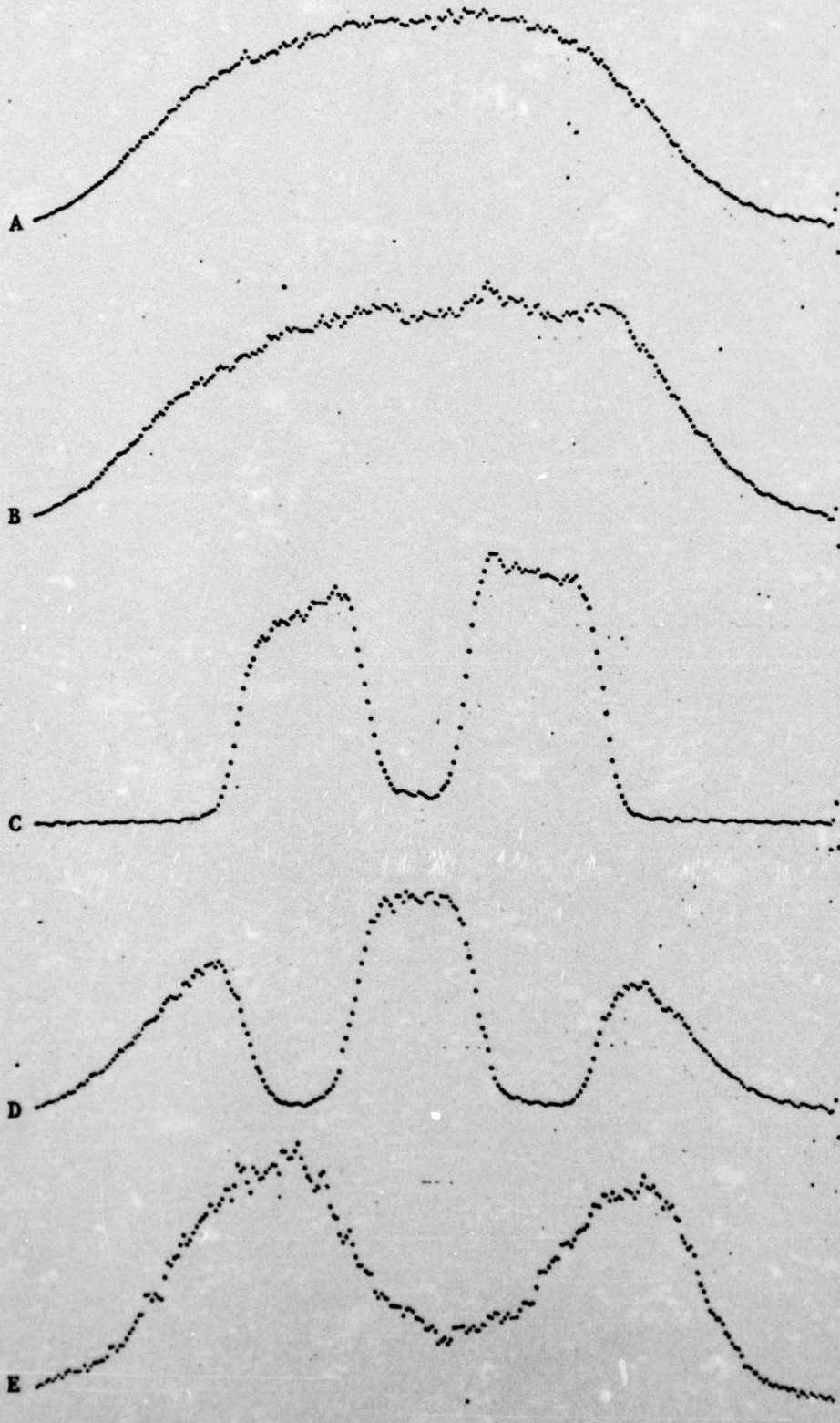


FIGURE 8

Same nozzle and wire diameter as that for Fig. 7. A - E are the spatially resolved concentration profiles downstream from the nozzle, as determined from the Raman intensity.



A — Concentration profile of N_2 (2331 cm^{-1} vibration) in air when no gas is flowing out of nozzle. D = 0.381 mm. Average of 20 laser firings. The sensitivity roll-off at two ends is evident.

B — Concentration profile of N_2 when air is flowing out of nozzle. D = 0.381 mm. Air pressure at entrance end of nozzle is 45 PSIG. Average of 10 laser firings.

C — Concentration profile of Freon-12, when Freon-12 is flowing out of nozzle. D = 0.381 mm. Freon-12 pressure at entrance end of nozzle is 20 PSIG. Average of 5 laser firings.

D — Concentration profile of N_2 when Freon-12 is flowing out of nozzle. D = 0.381 mm. Freon-12 pressure at entrance of nozzle is 20 PSIG. This should give the inverse profile of C. Average of 5 laser firings.

E — Concentration profile of O_2 (1555 cm^{-1} vibration) when flowing out of nozzle. D = 0.381 mm. The O_2 pressure at entrance end of nozzle is 60 PSIG. Average of 3 laser firings.

photography is not sensitive to such small changes in the refractive index caused by such subsonic ($\frac{1}{20}$ Mach #) and low Reynolds # (between 10 and 1,000) flow. This is particularly true for the O_2 jet into air, since the refractive index of O_2 is so similar to that of air, and the pressure of the gas just outside the nozzle is almost equal to the atmospheric pressure. (See Fig. 8E for the O_2 concentration profile.)

IV. CONCLUSION

In this ONR contract period, we have furthered the understanding of resonance Raman scattering in semiconductors. Two new phenomena were first observed by us, resonant cancellation in the TO Raman cross section and selective resonant enhancement in the two-phonon cross section when $\hbar\omega_i$ is near the indirect energy gap.

We have also designed and developed a new instrument for detecting the ultra-low light level Raman spectrum. The advantages of the PCDS have been realized in terms of the signal-to-noise ratio and the speed of data acquisition, particularly for low repetition pulsed lasers. We have demonstrated that spatially resolved gas concentration information can also be recorded by the PCDS. Specifically, by using one 1 msec ruby laser pulse, we have mapped out the concentration profile of a gas jet emerging from a nozzle with or without a wire placed in front of it. As a by-product of our research, we believe we have introduced a totally new diagnostic tool to study gas and combustion dynamics.

V. PERSONNEL ASSOCIATED WITH THE PROJECT

The Principal Investigator would like to gratefully acknowledge the help of ONR for the partial support of several enthusiastic graduate students and postdoctoral fellows who have contributed throughout various phases to the successful completion of this project. A list of these research associates follows.

	Present address
Graduate Students	
Philip C. Black	Yale, 5th year graduate student
Roger L. Farrow	Yale, 3rd year graduate student
Ph.D. Recipients	
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Paul B. Klein	Naval Research Laboratory
Joan L. Lewis	Naval Ship Research Development Command
James M. Ralston	Center for Naval Analyses
Jin-Joo Song	University of Southern California
Ronald L. Wadsack	Bell Laboratories
Postdoctoral Fellows	
Hiromitsu Masui	The Australian National University
Matthias Selders	Battelle Institute
Stanley S. Sussman	Lawrence Livermore Laboratory

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